High-Performance Electrodes for Medium-Temperature Solid Oxide Fuel Cells - Activation of Yttria-Doped Ceria Anode with Ni Electrocatalysts

M. Sugimoto*, H. Uchida, and M. Watanabe Laboratory of Electrochemical Energy Conversion, Yamanashi University, Kofu 400-8511, Japan

It is desirable to operate solid oxide fuel cells (SOFCs) at a medium temperature ($\sim 800^{\circ}\text{C}$) to overcome many serious problems such as a degradation of materials and a limited choice of materials, etc. However, two major obstacles must be solved to operate medium-temperature SOFCs. The first is to reduce an ohmic loss in the solid electrolyte. The second is to develop high performance electrodes because the electrode reaction rates must be slow down at such temperatures.

We have developed a porous catalyzed-reaction layer for medium-temperature SOFCs. $^{1\text{-}4}$ For the anode, mixed conducting samaria-doped ceria [(CeO₂)_{0.8}(SmO_{1.5})_{0.2}, denoted as SDC] was employed in combination with nanometer-sized Ru catalysts on the surface.

In order to enhance the anode performance further, we attempt to employ other mixed-conducting material with higher activity than SDC. For example, at 800° C, yttriadoped ceria (YDC) exhibits about 3 times higher electronic conductivity (σ_e) than that of SDC, while its ionic conductivity (σ_{ion}) is moderate, *i.e.*, it is lower than that of SDC but is comparable to that of 8 mol% YSZ. The high σ_e (> 10 S cm⁻¹ at 800° C) in the YDC anode is expected to reduce the ohmic loss and, probably, the overpotential even at high fuel utilization in SOFCs. Furthermore, Y_2O_3 is cheaper than Sm_2O_3 . Recently, we have found that the porous YDC anode exhibited higher performance than that of SDC at the operating temperature of 800° C to 1000° C. Highly dispersed Ru catalysts effectively enhanced the performance of the YDC anode.

In this paper, we report an activation of the YDC anode with highly dispersed (nm-sized) nickel electrocatalysts, which is more practical than Ru used so far.

Yttria-doped ceria $(CeO_2)_{0.7}(YO_{1.5})_{0.3}$ ($d=0.4 \mu m$) with and without Ni particle loading was used as the anode material. Onto an 8 mol% YSZ electrolyte disk, porous YDC anodes were prepared by screen-printing a YDC paste, followed by firing at 1250°C for 4 h. The YDC anode was impregnated with NiCl₂ solution, followed by heating at 1000°C for 1 h in air. The resulting NiO particles were then reduced to Ni nanocrystals in the fuel stream of the test cell. The steady state IR-free polarization characteristics of YDC anodes in humidified H_2 ($P[H_2O] = 0.042$ atm) were measured by a current-interruption method in a three-electrode configuration (with Pt anode and Pt/air reference electrode).

We have recently clarified that the high conductivities of both $\sigma_{\rm ion}$ and $\sigma_{\rm e}$ in the SDC anode layer are very important in reducing not only the ohmic loss but also the polarization loss. An area-specific ohmic resistance (R) was found to be a good measure to evaluate the contact resistance between SDC particles. Although a sinterability of YDC was found to be lower than that of SDC, a sintering of YDC anode layer at 1250° C for 4 h resulted in sufficiently low value of $R < 0.1~\Omega~\text{cm}^2$, which is comparable to that of optimized SDC anode reported previously.

Figure 1 shows the IR-free polarization curves for the YDC anodes with and without metal electrocatalysts (Ni or Ru). The polarization curves for the optimized SDC

anode (without metal catalyst)⁴ are also shown by dotted lines. In spite of the similar *R* values, the activity of YDC is higher than that of SDC at 800 to 1000°C. Hence, high electronic conductivity in the mixed conducting YDC plays an important role to enhance the anode reaction rate.

In order to activate the YDC anode, Ni catalysts were highly dispersed on its surface (0.5 mg/cm²). As shown in Fig. 1, Ni loading appreciably enhances the performance of the YDC anode especially at a low operating temperature. The current density at $\eta=0.1$ V was 0.4 A/cm² at 800°C, which is 1.6 times higher than that without catalysts. This performance is just same as that with Ru catalyst (0.1 mg/cm²). The Ni particle diameter, estimated from X-ray diffraction (XRD), was ca. 20 nm. It should be noted that a large amount of μ m-sized Ni is used in conventional cermet-type anodes. The present electrode has a distinct advantage, because the surface reaction on the mixed-conducting YDC anode can be activated by a small amount of nm-sized Ni electrocatalysts.

This work was supported by a Research Grant Project No. 00Y02008y from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

References

- 1. M. Watanabe, H. Uchida, M. Shibata, M. Mochizuki, and K. Amikura, *J. Electrochem. Soc.*, **141**, 342 (1994).
- 2. H. Uchida, N. Mochizuki, and M. Watanabe, *J. Electrochem. Soc.*, **143**, 1700 (1996).
- 3. H. Uchida, H. Suzuki, and M. Watanabe, *J. Electrochem. Soc.*, **145**, 615 (1998).
- 4. H. Uchida, T. Osuga, and M. Watanabe, *J. Electrochem. Soc.*, **146**, 65 (1999).
- 5. H. Yahiro, K. Eguchi, and H. Arai, *Solid State Ionics*, **36**, 71 (1989).
- 6. H. Uchida, M. Sugimoto, and M. Watanabe, in *Solid Oxide Fuel Cell VII*, The Electrochemical Society Proceedings Series, Pennington, NJ, in press (2001).

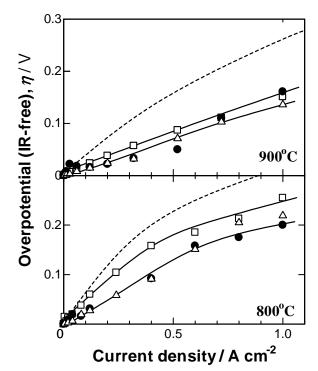


Figure 1. Polarization curves (IR-free, measured in humidified H_2) for SDC (dotted line), YDC (\square), Rudispersed (0.1 mg/cm²) YDC (Δ), and Ni-dispersed (0.5 mg/cm²) YDC (\bullet) anodes.